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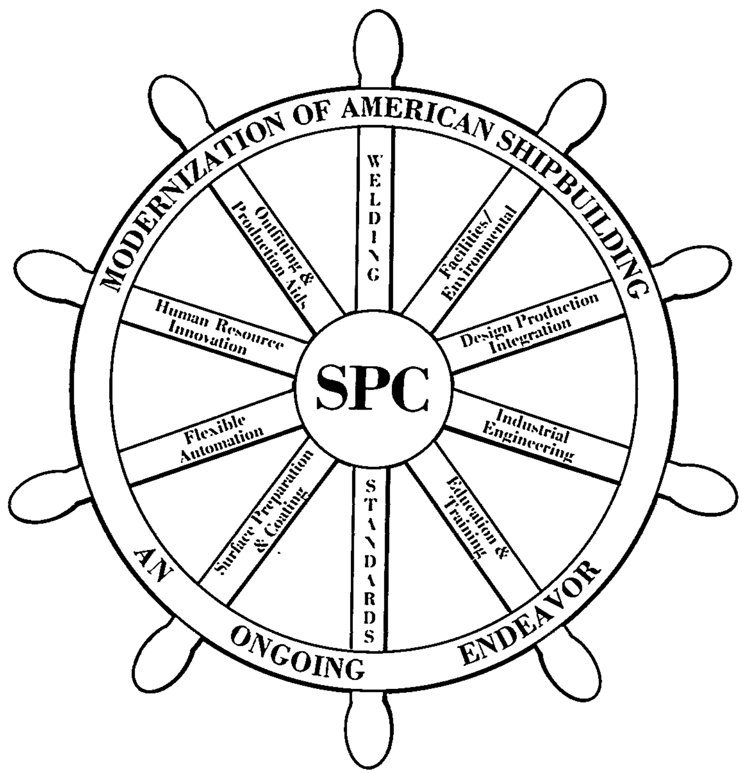

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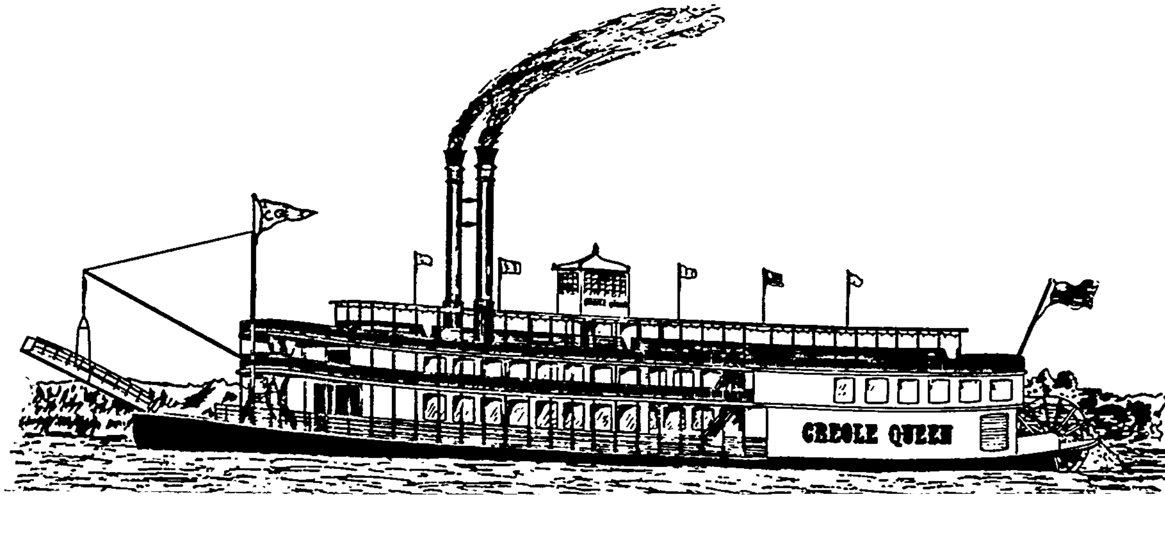

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A Low Toxicity Insulation Material for Shipboard Piping—Non-Halogenated Polyphosphazene Foam

No. 23

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ABSTRACT

A flexible, fire retardant, chlorine-free polymer foam with applications to pipe insulation has been tested for ship producibility. The new material, Non-Halogenated Phosphazene (NHP) foam, is based on Phosphorus-Nitrogen linkages (Phosphazene) with non-halogenated organic groups attached to produce selected engineering properties. The material tested is flexible, fire retardant, and produces less toxic combustion products than conventional plastic pipe insulation material.

Producibility tests have demonstrated the new material to be equivalent in handling characteristics to conventional material which uses PolyVinyl Chloride in its formulation.

The use of the new pipe insulation offers a prospect of removing over 1,400 pounds of elemental Chlorine from some surface ships now in production. Removal of Chlorine is in keeping with the objective of producing ships with improved fire protection and safety.

BACKGROUND - ORIGIN OF NON-HALOGENATED PHOSPHAZENE

The degeneration of Halogenated hydrocarbons such as Vinyl Chloride to toxic and corrosive products when burned makes elimination of Chlorine- and Fluorine-containing elastomers from ships a worthwhile objective. Replacement of such compounds with Non-Halogenated and more flame resistant materials has been recognized as a means of enhancing personnel safety and improving the passive fire protection status of ships.

Research in this area has resulted in technology which provides alternatives to the use of Chlorine to form strong, stable bonds with Carbon, Nitrogen, Oxygen, and Hydrogen in elastomers. From that background, a new family of compounds known as Poly-Phosphazenes, which utilize the Phosphorus=Nitrogen bond (P=N) as an inorganic basis for flexible long chain polymers, has been developed. These compounds exhibit a number of useful properties, including low temperature flexibility, good flex-fatigue, sound dampening, flame resistance, low smoke production, and resistance to oil, in addition to greatly reducing toxic gas emissions.

DEVELOPMENT OF NON-HALOGENATED PHOSPHAZENE (NHP) FOAM AS AN INSULATION MATERIAL

One form of the chemical family, Polyaryloxy Phosphazene, has been demonstrated to be producible as low density, closed cell foam. The product is now in production by at least one U.S. producer as foamed slabs and tubing. It exhibits the properties described above, as well as low thermal conductivity and low toxicity of pyrolysis products. The acronym, NHP, will be used to refer to the Non-Halogenated Polyphosphazene foam used to generate data on which this report is based.

The production of NHP as a foamed elastomer in tubes suitable for pipe insulation and in sheets for general insulation has reinforced shipyard interest in Chlorine-free sound dampeners and insulations because the combinations of low moisture absorption, low smoke, and low fume toxicity offer distinct advantages for both surface ships and submarine applications.

FUME AND TOXICITY TESTING

Flame and fume toxicity testing of Phosphazene compounds has been performed at the University of Pittsburgh, Graduate School of Public Health, and the Department of Metallurgical and Materials Engineering; test results have been published by Lieu, Magill, and Alarie [1]. In that study, the LC50 for laboratory animals was compared with the LC50 of Douglas Fir. The LC50 for the Non-Halogenated foam was 21 grams; for the wood, the value was 37 grams. The LC50 is the sample loading which provides a concentration of thermal degradation products resulting in 50%

mortality of test animals under the test conditions. In practical terms, the toxicity products from the Non-Chlorinated foam were determined to be similar to the irritating effects of the smoke and fumes produced by burning a common specie of wood. Alarie and co-workers estimated that smoke and fumes from Poly-Vinyl Chloride rubber products are approximately ten times more toxic than Poly-Phosphazene [2]. Another study involving human exposure concluded that tolerable levels of respiratory or lachrymal (tears) distress are produced by brief human exposure to Poly-Phosphazene smoke [3]. Reduced to practice in terms of ship safety, this means that significantly longer times may be made available for fire-fighting personnel to gain control of a fire in or adjacent to a compartment which contains Non-Chlorinated Polyphosphazene foam insulation rather than Poly-Vinyl Chloride foam. In contrast, a fire in a compartment with PVC insulation can be expected to emit toxic levels of Chlorine and Chlorinated gasses.

Further indication of tow toxicity of pyrolized Non-Halogenated foam relative to currently used PVC-Nitrile foam is shown in published data and in independent tests.

Comparative tests of NHP and PVC insulation reported show the following typical values:

	Eypel^{tm} A (NHP)	Typical MIL-P-15280 (PVC)
Acid Gas Generation (mg HydroChlorine Acid/gm per MIL-C-24640)	0	70
Halogen Content, % by weight	< 0.2	> 14

SHIPYARD TESTING OF THERMAL STABILITY, CHLORINE GAS EMISSION AND SMOKE

Under normal conditions, the Chlorine in conventional insulation is securely bonded chemically within the Hydrocarbon molecules; however, when heated, the molecules pyrolize, break down, produce smoke, and release toxic fumes, including Chlorine gasses and potentially corrosive solids as smoke particles and ash. The Chlorine combines readily with moisture in the atmosphere to form Hydrochloric (HCL) acid gas. Laboratory measurements were made to determine the actual temperature at which a sample of conventional PVC/Nitrile insulation material would just start to pyrolize and emit Chlorine and Hydrochloric acid gas without direct flame on the material. To make this measurement, a 6"x6" piece of 1/2" thick aluminum plate was drilled from the edge to receive a laboratory thermometer. A 1"x1"x3/4" piece of insulation was placed on the plate, and to concentrate the fumes, a pyrex funnel was inverted over the sample. A Bunsen flame was placed under the plate and the plate was heated until the sample began to decompose. Flame was prevented from making direct contact with the sample. Emissions from the outlet of the inverted funnel were aspirated into a 2-20 PPM Hitagawa 1095B "Hydrogen Chloride Length-of-Stain Detector Tube". Several repetitions were made to determine that the starting temperature for the emission of HCL acid from the PVC/Nitrile foam was 335 degrees C (635 degrees F). Emission of black smoke, even without impingement of flame, began at the same time that Chlorine was detected.

Chlorine is present at one step of processing of NHP foam, and for that reason, the test was repeated for an equivalent NHP foam sample. A light trace of smoke was observed at 350 degrees C, but no residual Chlorine was detected up to and including 355 degrees C (671 degrees F). The test was stopped at that temperature to prevent damage to the lab equipment. Further efforts to force detectable levels of Chlorine gas out of the Phosphazene foam by direct application of the flame also failed to produce an indication on the Hitagawa Test Tubes.

The presence of a high percentage of Chlorine content in the conventional foam sample and the absence of Chlorine in the Phosphazene was further demonstrated by the classical Bielstein test. A Copper wire was heated in the Bunsen flame. The hot Copper wire was rubbed on the sample to produce and pick-up pyrolysis products. The contaminated Copper wire was then transferred directly into the Bunsen flame. A green fluorescence in the flame would indicate the presence of Chloride. The PVC/Nitrile material produced a bright green color, as expected, since Poly-

Vinyl Chlorine is a major component of the material. On the other hand, the NHP sample did not produce any detectable green color in the flame, indicating very low or no Chlorine present.

FIRE RETARDANCY OF NHP FOAM

Direct flame was then applied to both materials using an Oxygen-rich acetylene flame to make a visual comparison of the flaming, smoke producing, and charring properties of both types of insulation.

Both materials produced observable secondary combustion with yellow flame and black smoke. The PVC/Nitrile sample of conventional insulation flamed much more vigorously and produced much more black smoke than the NHP foam. Both materials were self-quenching when the flame was removed, and both produced charring and black powder residue to about the same extent. Neither sample showed any tendency to melt and drop hot or burning plastic, as would occur with a thermoplastic polymer such as Polyethylene foam.

The relatively greater flaming and flaring of the PVC is clearly seen when a Bunsen burner flame is applied directly to foam samples. The PVC foam reaction is distinctly exothermic, and supports the spread of combustion, whereas the Poly-Phosphazene is slower to flame, and then produces only slight initial exothermic heat, becoming non-contributing to the fire.

Flame retardant properties of Poly-Phosphazene were found to be superior to conventional insulation in the National Bureau of Standards Quarter Scale Test. This test method was developed to test flame and heat propagation characteristics of candidate coatings and insulation for ship compartments. In this test, a steel box is lined with test material and a methane burner is ignited in one corner of the box. Time after ignition to flash-over of combustible emissions from insulation is measured, and smoke generation is observed. In the test performed by Mueller, Arroyane and Associates [3] PVC/Nitrile foam flashed over quickly with a 640 BTU/minute Methane flame [3]. Paper placed on the floor of the box, which was two feet high, ignited from the heat of the chamber and flames flared out of the transom of the "door" of the box.

The Poly-Phosphazene did show initial combustion of some volatile emissions, but stabilized in about one minute, after which time flame did not spread beyond the direct path of the Methane burner in the corner of the box. The NHP foam did not support combustion.

After the ten minute duration of the test, the thermocouple mounted on top of the box recorded a maximum temperature of 131 degrees F (55 degrees C) [3]. A video tape of the PVC foam and NHP foam Quarter Scale Test was made, and is available.

HANDLING CHARACTERISTICS AND SHIPYARD PRODUCIBILITY

In order to test for producibility, an eight foot section of the 2" NPS Copper pipe was used in the Ingalls shop as a mock-up of production pipe. Both standard and the new materials were used to insulate the pipe, using standard shipyard processes.

Insulation of a Typical Pipe

One segment of Copper pipe was insulated using standard tubular PVC/Nitrile and two other segments of pipe were insulated with NHP foam. One pipe segment was insulated with tubular NHP material, and the other used 1/2" thick flat sheet formed around the pipe. After wrapping around the pipe, the slitted edges of the insulation were bonded together. The adhesive used for both materials was the standard solvent-based MIL-A-3316 which is normally used for this purpose. The adhesive bonds were verified as acceptable by tensile loading across the bonded seams to failure. In both types of material, the failures always occurred as base material tearing rather than adhesive failure of the bonded joint.

During cutting and trimming of the two types of foam, it was observed that both materials were subject to tearing on the edges if sharp edges on cutting tools were not maintained. The NHP foam was slightly more susceptible to tearing than the PVC foam.

Repairability Test

Repairability was considered an important producibility factor because of the need for occasional partial rip-out for repairs to piping. Because of the relatively low tensile strength of both types of material tested, comparisons of repairability were made by ripping and then patching tears over 3" long in both materials.

The tears were made through the thickness of the material, and patched with the same adhesive used to join sections in production. The adhesive used is quick curing, and repair is performed very quickly. The insulation craftsman reported that there is no difference in repairability of NHP and PVC insulation material.

Typical tensile strength of the NHP appears to be somewhat less than the PVC; however, both materials are subject to tearing. For that reason, it is standard practice to apply a protective lagging of glass cloth over insulation in the way of heavy traffic and in all areas where personnel and hardware are likely to cause damage. For that reason, response of the new material to lagging procedures and materials was also tested.

Installation of Standard Lagging Materials

Subsequent to cutting, fitting, and installing the two types of insulation on the Copper pipe, both test areas were wrapped with the standard lagging materials -- MIL-C-20079 glass cloth, and impregnated with MIL-A-3316 water-based sizing compound. The lagging material is from Vimasco Corporation of Nitro, West Virginia. According to the insulation craftsmen who performed the installation, there was no significant difference in handling characteristics and response of the NHP relative to the lagging materials and application.

No effort was made to fabricate an irregularly shaped covering as would be needed for a valve; however, it can be inferred that the workability of the flat 1/2" thick Poly-Phosphazene foam sheets applied to pipe would be equally applicable to valve bodies or other components, and no producibility problems would be expected.

COMPARISON OF NHP FOAM WITH OTHER INSULATION MATERIAL

Other important physical properties compared indicate that the new Non-Chlorinated foam is equal to or better than the PVC/Nitrile elastomer now generally used for pipe insulation. For example:

Property	NHP Test Result/Comparison
Density	4.5 lbs/ft^3 (density can be controlled by cell size) material
Compression Set	equal to PVC foam
Thermal Conductivity	equal to PVC foam
R Value	equal to PVC foam

The availability of equivalent Non-Halogenated insulation materials other than Phosphazene has been considered. Technically, foamed Polyimide and Silicone compounds could become candidate materials to replace PVC foam for ship piping insulation. However, the available information indicates that Polyimide and Phosphazene are close together in cost, but that Polyimide is an open cell foam which retains water. The NHP has already been produced and tested in both sheet and tubular form. Polyimide foam has not been demonstrated producible in flexible tubular foam for pipe and valve insulation; the Silicone-based material is expected to be more costly than either Polyimide or Poly-Phosphazene.

WATER RETENTION OF INSULATION MATERIALS

Three basic types of material are generally used to insulate piping for cold liquids and gasses in surface combat ships; open cell foam, closed cell foam, and fibrous materials.

When all other factors are equal, closed cell insulation materials for shipboard piping offer the advantage that it will not absorb and retain a significant amount of water. Retention of water adversely affects two important properties -- density and thermal conductivity. Several currently used insulation materials were tested for tendency to absorb, to drain, and to retain water. Four materials were compared: PVC-Nitrile (closed cell), Non-Halogenated Phosphazene (closed cell), Polyimide Foam (open cell), and layered glass fiber batting.

Samples of the tested materials were tare weighted on a lab balance and then subjected to water droplets impinging on cut edges. The droplets were applied at a rate of approximately one per second for thirty minutes. The PVC-Nitrile and the NHP did not produce a significant weight increase. A three cubic inch sample of Polyimide foam increased its weight by 296%; the 4.5 cubic inch glass fiber batt increased its weight by 278%. Note that the dry glass had a density twice that of dry polyimide and absorbed about twice as much water under the similar conditions.

A worst case test of water absorption and retention was performed by immersing the four samples in water for one hour. The samples were hung in air and allowed to drain for 16 hours, then reweighed. As seen in the table below, the PVC-Nitrile and NHP foam retained no water. The glass batt and the polyimide foam retained the equivalent of 7.44 and 14.88 pounds per cubic foot, respectively, even after 16 hours of hanging in the air to drain.

WATER RETENTION TEST OF SEVERAL
COMMONLY USED INSULATION MATERIALS

Material	Sample Size	Tare Weight (gm)	Weight After Immersion (gr)	Weight After 16 Hour Drain (gm)	Wt/ft^3 (Increase)
Glass Fiber Batting	1-1/2"x1-1/2"x 2"	1.4	22.9	18.9	14.8 lbs/ft3
Polyimide Foam	1-1/4"x3-1/4"x 3/4"	0.6	9.4	9.4	7.44 lbs/ft3
PVC-Nitrile	3-1/2"x1-1/2"x 3/4"	4.2	4.4	4.2	0
NHP	6-1/2"x2"x1/2"	8.6	8.9	8.6	0

COST FACTORS

Details of comparative costs of NHP versus conventional pipe insulation are not available at the time of this writing. The producibility exercise described above indicates that labor costs to install would be essentially the same for NHP as for PVC-Nitrile. Initial cost of the NHP material would likely be greater than for PVC-Nitrile and to maintain cost equivalence, innovative methods of reducing labor cost to install are being evaluated. One approach being considered is the use of an easily installed, removable protective outer jacket to replace the manually applied lagging materials. One such material has been tested for resistance to damage from hot welding slag and found to be equal to or better than conventional lagging. The reduction in labor using a locking closure insulation shield would be greater than 50% and would also reduce scrap, since removed insulation could be easily reinstalled after repairs.

QUANTITY OF CHLORINE REMOVAL

An estimate of potential for Chlorine removal is given below. The estimate is based on (1) nominal density, (2) percent by weight of Chlorine in PVC-Nitrile and (3) typical quantities of hot and cold water pipe insulation used in today's surface ships. The density of PVC-Nitrile is over 4 lbs/cu.ft., Chlorine percent by weight is 14%, and today's surface ships typically use over 1,000 pounds of such insulation per thousand tons of displacement. Therefore, for a 10,000 ton ship, a conservative estimate of potential yield of Chlorine from fire is over 1,400 pounds as elemental Chlorine gas. If combined with atmospheric moisture to form HCl.H2O gas, the quantity of gas is significantly greater than 1,400 pounds by weight.

JUSTIFICATION FOR USE - SHIP SURVIVABILITY

The principal justification for consideration of non-chlorinated insulation for ships is found in the increased effectiveness of active and passive fire protection afforded by the new material. Flame retardancy tests and flashover tests show that PVC foam flashes over in a few minutes, allows much more rapid spread of fire, and produces more smoke than NHP foam.

CONCLUSION

A new, flexible NHP foam insulation material for piping has been tested at Ingalls. The material, Non-Halogenated Phosphazene foam, does not support combustion, produces less smoke, and, unlike PVC/Nitrile insulation, does not emit toxic Chlorine gasses when heated. The material has been shipyard tested and meets insulation requirement of MIL-P-15280H, and producibility requirements for shipyard insulation of water piping systems.

The new material provides a potential for removal of over 1,400 pounds of elemental Chlorine from a 10,000 ton ship and proportional amounts for other ships.

The material is currently being evaluated for use on hot and cold water systems on surface ships.

ACKNOWLEDGEMENT

The late Mr. Michael McGowan is recognized and appreciatd for his contribution to this project. Mr. McGowan initiated the project while a member of the Ingalls Advanced Technology Group under the Independent Research and Development program prior to joining the Alcoa Research and Development Center. He was a productive and dedicated researcher, and was responsible for numerous contributions to improvements in ship safety.

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